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FEASIBILITY STUDY: HOLLOW PLASTIC SPHERES TO INCREASE HYDRAULIC FLUID COMPRESSIBILITY

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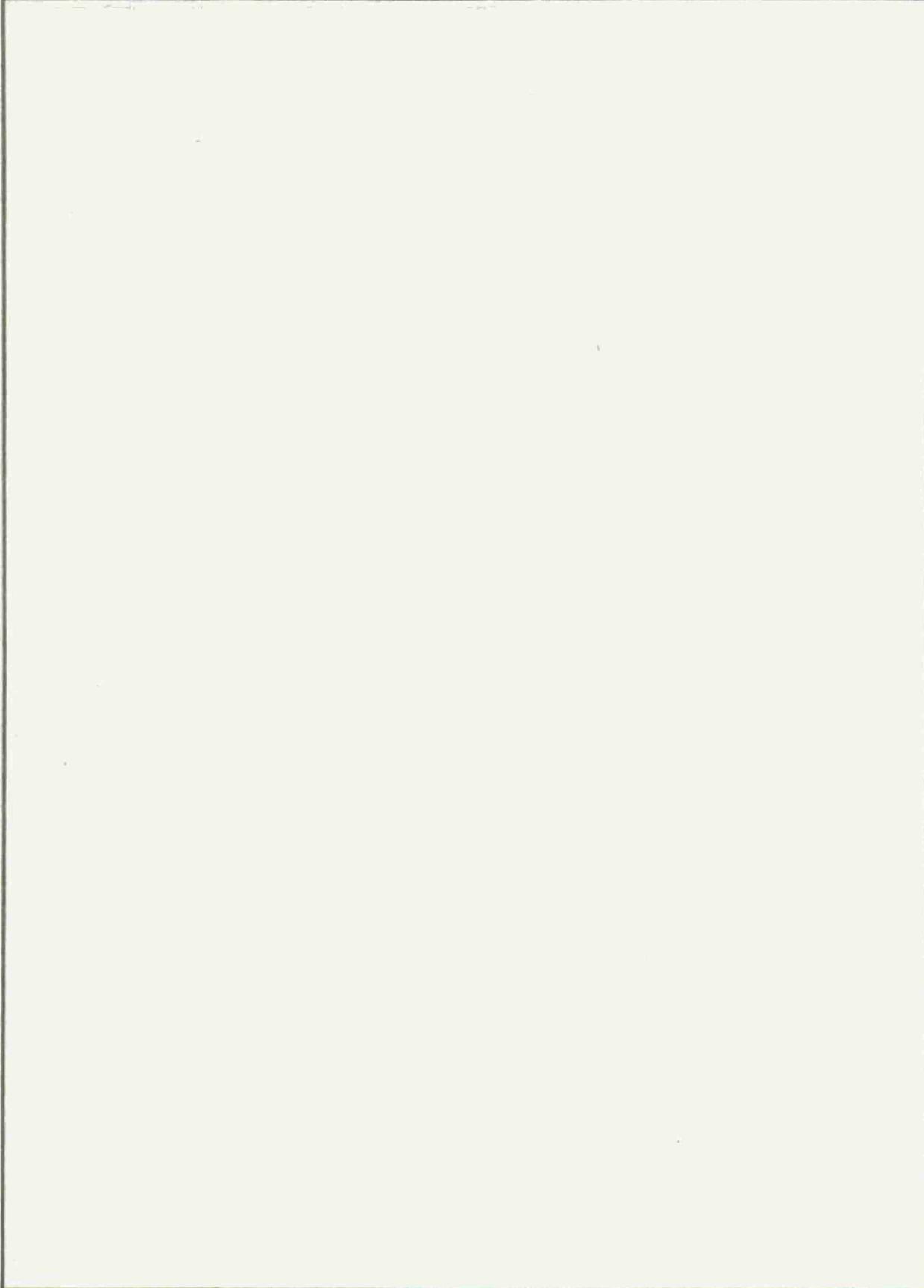
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report documents a study on the feasibility of using sub-micron size hollow plastic spheres as an energy absorbing medium in the fluid of a compressible fluid recoil mechanism for field artillery. The study identifies the properties of a polymer which theoretically will increase the compressibility of a recoil fluid.		

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SUMMARY

The theoretical feasibility of using micron-size hollow plastic spheres (HPS) suspended in a hydraulic fluid (Dow Corning 200 Silicone fluid) to increase its compressibility has been investigated. A vendor search of suppliers of HPS revealed only one source of manufactured HPS with controlled wall thickness, Rohm and Haas, Inc.

An engineering analysis of strain and compressibility as applied to a hollow sphere indicated that three factors control the compressibility of the sphere:

- Elastic modulus
- Poisson's ratio
- Relative wall thickness.

Using literature values of these properties, the theoretical compressibilities of the HPS made from several different polymers were calculated. These compressibility calculations and analyses are intended to serve as a guide in selecting appropriate HPS candidates. The polymers chosen were those Rohm and Haas's chemist indicated could possibly be made or were known to be compressible materials or were those whose properties were known well enough to calculate their compressibilities. These materials were polystyrene, low density polyethylene, polyvinylidene chloride, and fluorinated ethylene propylene (FEP, Teflon) copolymer. Of these four polymers, low density polyethylene is the most compressible. Polyethylene, however, is not currently made as a hollow plastic sphere and the costs to produce it are not justified for the first set of experiments in which the concept using HPS will be tested. Rohm and Haas manufactures micron-size polystyrene based HPS. These spheres are recommended for the first experiment because they are available and can be provided at the lowest cost. According to the compressibility calculations, polystyrene HPS do not appear to be very compressible. Experimental testing, however, will indicate how realistic the calculations are.

In addition to the engineering analysis, the chemical resistance or chemical compatibility of the candidate materials for HPS were evaluated. An analysis of polymer properties was included as an aid in selecting the appropriate HPS. Polystyrene HPS, while again not expected to be very compressible are anticipated to be chemically compatible with the silicone hydraulic fluid. Recommendations from the polymer properties include using Teflon-like polymer particles for increasing fluid compressibility.

At this point in the overall program, the most cost effective material to use with silicone hydraulic fluid is polystyrene HPS. Polystyrene HPS are recommended to test the concept of using micron-size HPS suspended in silicone hydraulic fluid in the bench scale model of the recoil mechanism.



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1. INTRODUCTION

In 1976, the US Army Armament Research and Development Command (ARRADCOM) Large Caliber Weapons Systems Laboratory (LCWSL) proved the feasibility of a radically new recoil design concept. In addition to employing fluid as a means for dissipating energy, the new concept uses the fluid as an energy storing medium. When brought to fruition, the new design could result in high reliability, availability, and maintainability (RAM) characteristics, as well as greater simplicity and subsequent overall cost reductions.

ARRADCOM has concluded from preceding studies that a fluid compressibility of 8 to 10 per cent at maximum pressure and minimum temperature would be ideal for use in artillery recoil mechanisms employing the new concept. When such a fluid compressibility is reliably attainable, conventional recoil spring and damping mechanisms can be replaced by the simplified fluid recoil mechanism.

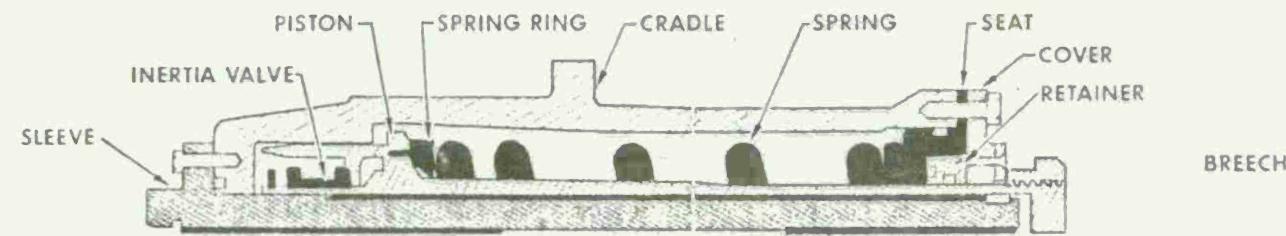
2. BACKGROUND

Current designs of artillery recoil mechanisms employ a spring-loaded hydraulic damping system. The force resulting from a firing and imparted by the barrel is absorbed partially by the compression of a coil spring and partially by a throttling action of hydraulic fluid flowing through an annular orifice. The gun barrel is returned to its battery position by the release of the stored energy in the compressed spring.

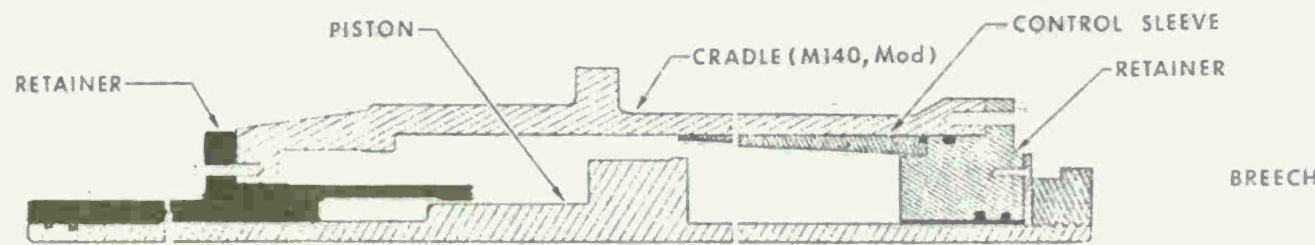
Utilizing the attributes of a compressible hydraulic fluid, the ARRADCOM LCWSL has designed a simplified recoil mechanism, presently designated as the compressive fluid recoil mechanism (CFRM), shown in Figure 1. This design eliminates the need for a coil spring by utilizing the hydraulic fluid's compressibility and the resultant energy stored therein. Opposing the gun's firing action, the retracting barrel causes compression of the fluid. The resultant fluid pressure (stored energy) returns the gun barrel to the battery position by means of hydraulic force.

No fluid has been found which fully satisfies compressibility and temperature stability requirements. To reduce the volume of fluid required and consequently the recoil stroke, a fluid compressibility of 10 per cent at 3.5×10^7 Pa is desired. Of all the available fluids evaluated by LCWSL, Dow Corning 200 Silicone was found to be the most suitable. At a temperature of 25°C , when a compressive force of 3.5×10^7 Pa

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M140 RECOIL MECHANISM



COMPRESSIBLE FLUID RECOIL MECHANISM

FIGURE 1. M140 RECOIL MECHANISM AND COMPRESSIBLE FLUID RECOIL MECHANISM

is applied, this fluid compresses approximately 3.5 per cent. At -45°C however, its compressibility is approximately 2.1 per cent. This 40 per cent change in the fluid's compressibility over the temperature range 25°C to -45°C is undesirable.

A proposed way to increase the compressibility while reducing the volume of fluid is to use a fluid mixture in which hollow plastic spheres have been suspended.

3. PURPOSE AND SCOPE

ARRADCOM has tasked the NASA/National Space Technology Laboratories (NSTL) Engineering Laboratory to conduct a study to determine the feasibility of using very small hollow plastic spheres in hydraulic fluid for the purpose of:

- Increasing the compressibility of hydraulic fluid.
- Decreasing the amount of fluid required in the compressible fluid recoil mechanism.

The fluid to be considered is Dow Corning 200 Silicone (DC200) and the spheres are to be micron (1×10^{-6} meter, micrometer \equiv micron) size.

4. APPROACH

4.1 Environment. The required operating environment for compressible hollow plastic spheres in a compressible hydraulic fluid used in the CFRM's is as follows:

- Temperature - -45.5°C to 65.5°C
- Recoil Cycle Time - 600×10^{-3} seconds
- Pressure Range - 0 to 3.5×10^7 Pascals
- Hydraulic Fluid - DC 200, $10^{-5} \text{ m}^2/\text{s}$ viscosity (58.8 Saybolt seconds* @ 37.8°C)

4.2 Vendor Search. A vendor search was conducted to locate sources of hollow plastic spheres, the plastics used in their construction, and the cost required to manufacture them.

Sixty-seven American companies and seventy-nine foreign companies were contacted. The geographical distribution is shown in Table 1, and the U.S. and foreign companies contacted are listed in Appendices A and B, respectively. Addresses and telephone numbers of thirty-seven companies that responded are listed in Appendix C.

4.3 Commercial Production of HPS. The Rohm & Haas Company presently produces HPS of primarily polystyrene which are used in the formulation of a non-film forming emulsion polymer. The HPS are suspended 40 per cent by weight in water solution. Designated as Opaque Polymer E-1742, the polymer emulsion is used as an additive for trade sales paints. The diameter of the polystyrene hollow spheres ranges from 4×10^{-7} to 6×10^{-7} meter. The void volume of the spheres is 20 per cent of the total volume. Wall

*Saybolt - Universal viscosity = 58.8 seconds

TABLE 1. Vendor Search

COUNTRY	NUMBER OF COMPANIES CONTACTED
U. S.	67
CANADA	5
BELGIUM	17
DENMARK	4
ENGLAND	10
LUXEMBOURG	1
NETHERLANDS	7
SWEDEN	11
WEST GERMANY	8
JAPAN	5
TAIWAN	11
TOTAL	146

thickness averages 70 per cent of the diameter. According to Rohm & Haas, photo-micrographic analyses show exceptional uniformity of the spheres. Rohm & Haas can produce polystyrene HPS commercially by utilizing their techniques and equipment presently used to produce Opaque Polymer E-1742.

Polystyrene HPS supplied in dry form will initially cost considerably more than the aqueous solution because a research and development (R&D) effort would be required to accomplish the following:

- Produce spheres in a dry form.
- Surface treat spheres to maintain sphere separation and avoid jelling and/or congealing in silicone fluid (make the spheres compatible with silicone fluid).
- Obtain optimum size uniformity in the deliverable dry product.

Among the other polymers investigated, polyethylene appears promising; polyethylene HPS, however, cannot be made without extensive R&D. Since the goal at this point is to use a polymer to test the concept of HPS in fluids, the extra costs to obtain polyethylene HPS are not warranted.

Other polymers have been used to manufacture HPS. Most of these spheres, e.g., phenolic balloons, are too rigid and brittle to be used to increase the compressibility of fluids. In addition to Rohm and Haas, several other companies manufacture HPS, e.g., Union Carbide, Minnesota Mining and Manufacturing (3M), Pittsburgh Plate Glass, and Emerson-Cumming. These companies either do not control the dimensions and wall thickness of the end product or they manufacture polymers more brittle than polystyrene.

5. LITERATURE SEARCH

A literature search was conducted. From the subject guide to books in print, card references, Dialog I.R.S. and NASA/Recon (computer search of technical references), a list of books and reports was compiled and reviewed, and is included with key words and subject utilization in Appendix D.

The use of HPS as a means for increasing hydraulic fluid compressibility is an uncharted field of engineering. Literature covering this approach is practically non-existent. The literature search, however, produced sufficient information to conduct a reasonably comprehensive feasibility study in which numerous polymers were screened and categorized as candidate materials for HPS usage. Books found to be most useful in the analyses are indicated by an asterisk on the reference page.

6.

MATERIAL PROPERTIES

The proposed enhancement in compressibility when hollow plastic spheres are added to hydraulic fluids relies on both the physical and chemical properties of the polymers or plastics chosen. A short discussion of the more important pertinent properties of polymers is presented and examples of the values of the parameters related to these properties are included for some likely polymers. The polymers chosen were those whose compressibilities had been investigated as described in Section 8. The material properties of polymers, including compatibility with fluids, depends upon the way in which the polymer is made and treated.

Although values for several of these polymer parameters are available in the literature, it must be recognized that those values are for only the particular type of polymer made and tested in a specific way. Unfortunately, often the specific polymer including the synthetic process and polymer form, and the details of the tests are not specified. The values given in tables actually will represent only a general range of values for a particular parameter. One point, especially, must be made: most of the information is for polymer sheets and not for hollow plastic spheres. In the absence of specific experimental information and testing on hollow plastic spheres, the parameter values listed are only indications of approximate ranges and trends.

6.1 Compressibility and Flexibility. Polymer properties depend on the structure of the polymer including:

- The degree of branching of the polymer chains.
- The degree of cross-linking between chains.
- The degree of amorphous character.
- The degree of crystallinity in the polymer.

These properties are reflected in the temperature characteristics of the polymer. The glass transition temperature (T_g) demarks the boundary between flexible and rigid forms of a polymer. Below T_g the polymer is rigid and glass-like, and above T_g it is mostly amorphous or rubbery. The melting point (T_m) is the point at which the polymer melts. Polymers, such as FEP, Teflon may have no T_g because they are very crystalline; they will become soft, however, near their melting point.

In searching for a compressible polymer, amorphous polymers generally will be more compressible than glass-like polymers. The greater the difference between the T_g and T_m , the greater the range over which a polymer is flexible. Figure 2 illustrates the various differences between T_g and T_m for several polymers and the stated operating range for the recoil mechanism. Figure 3 illustrates the change in compressibility of polymers as a function of temperature. The sharp inflection of vinyl near 50°C is indicative of the change expected near a polymer's glass transition point. The lack of inflection for low density polyethylene is an indication that the polymer is crystalline.

6.2 Crystalline versus Amorphous. As noted in the previous section, polymers can be characterized by the amount of amorphous properties versus the degree of crystallinity they possess. The degree of crystallinity affects the elastic modulus because the individual crystals act as rigid fillers in an amorphous matrix. This effect is most notable above the glass transition temperature when the matrix is rubbery. Below the glass transition temperature the matrix has approximately the same rigidity as the crystals.

When an amorphous polymer is compressed, the polymer chains reorient themselves into a more compact arrangement. Once they have oriented themselves into a space-efficient order, further compression requires overcoming intermolecular forces, which increase very rapidly as the distance between molecules decreases. When a fully crystalline polymer is compressed, no rearrangement occurs; therefore, compression requires overcoming intermolecular forces alone. Amorphous polymers are more flexible (i.e., deform more easily) than crystalline polymers. Curing a polymer may decrease its flexibility by increasing the probability that small crystals will be formed on the surface of the polymer and grow into the rest of the polymer, thereby increasing its crystallinity. Thus when choosing a polymer for compressibility, polymers which have not been cured are preferred.

6.3 Cross-Linking. A cross-linked polymer is one in which molecular bonds link different polymer chains to each other and build a large, three-dimensional molecule. Cross-linking generally improves the strength and stability of a polymer. It also increases the polymer's brittleness. Below the T_g of a polymer, or if the polymer has no T_g , the degree of cross-linking has a minimal effect on its elastic modulus. Above the T_g , cross-linking can have a significant effect on the elastic modulus of polymers. This effect is depicted in Figures 4 and 5.

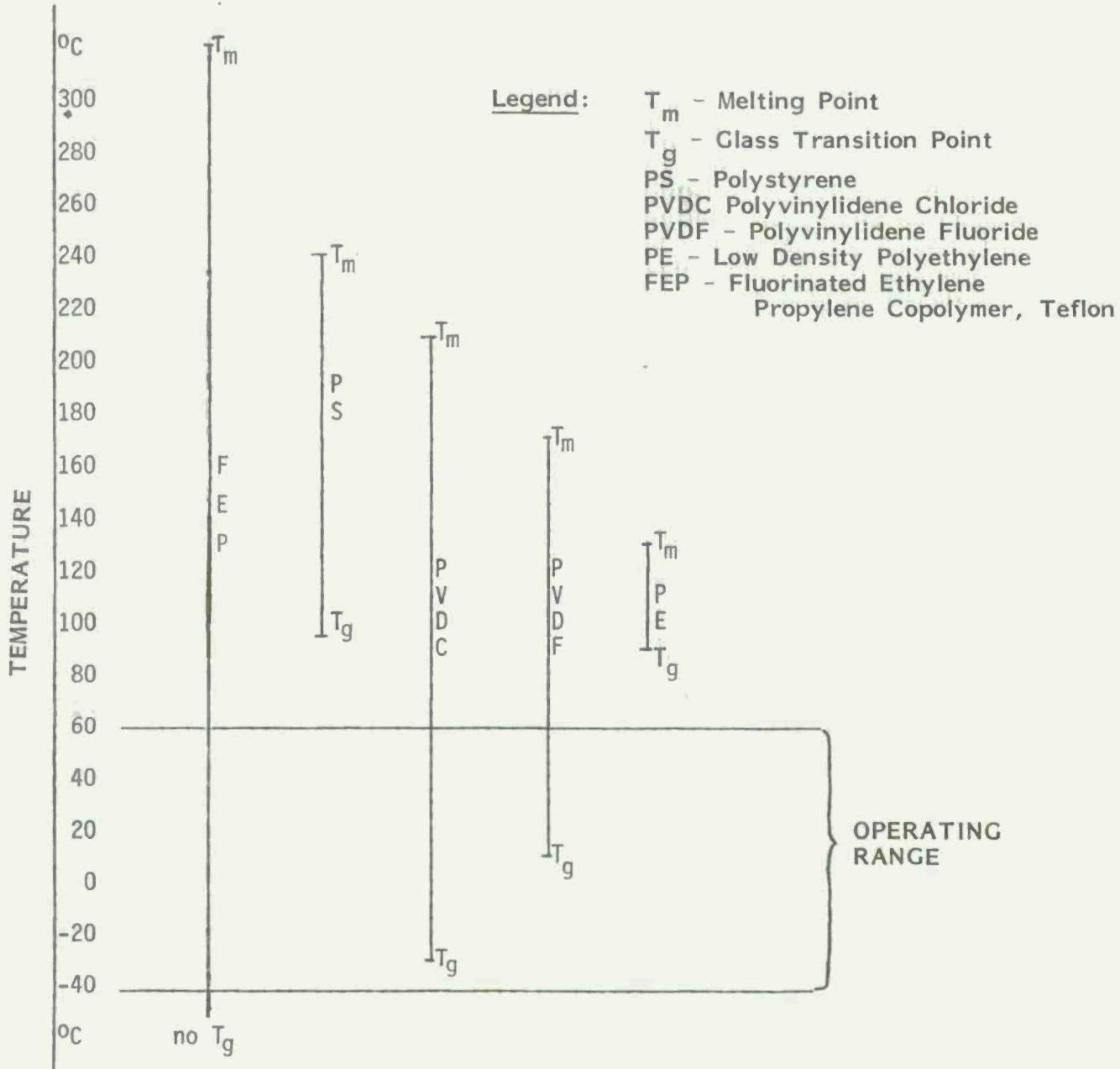


FIGURE 2. CHARACTERISTICS OF SEVERAL POLYMERS AS A FUNCTION OF TEMPERATURE

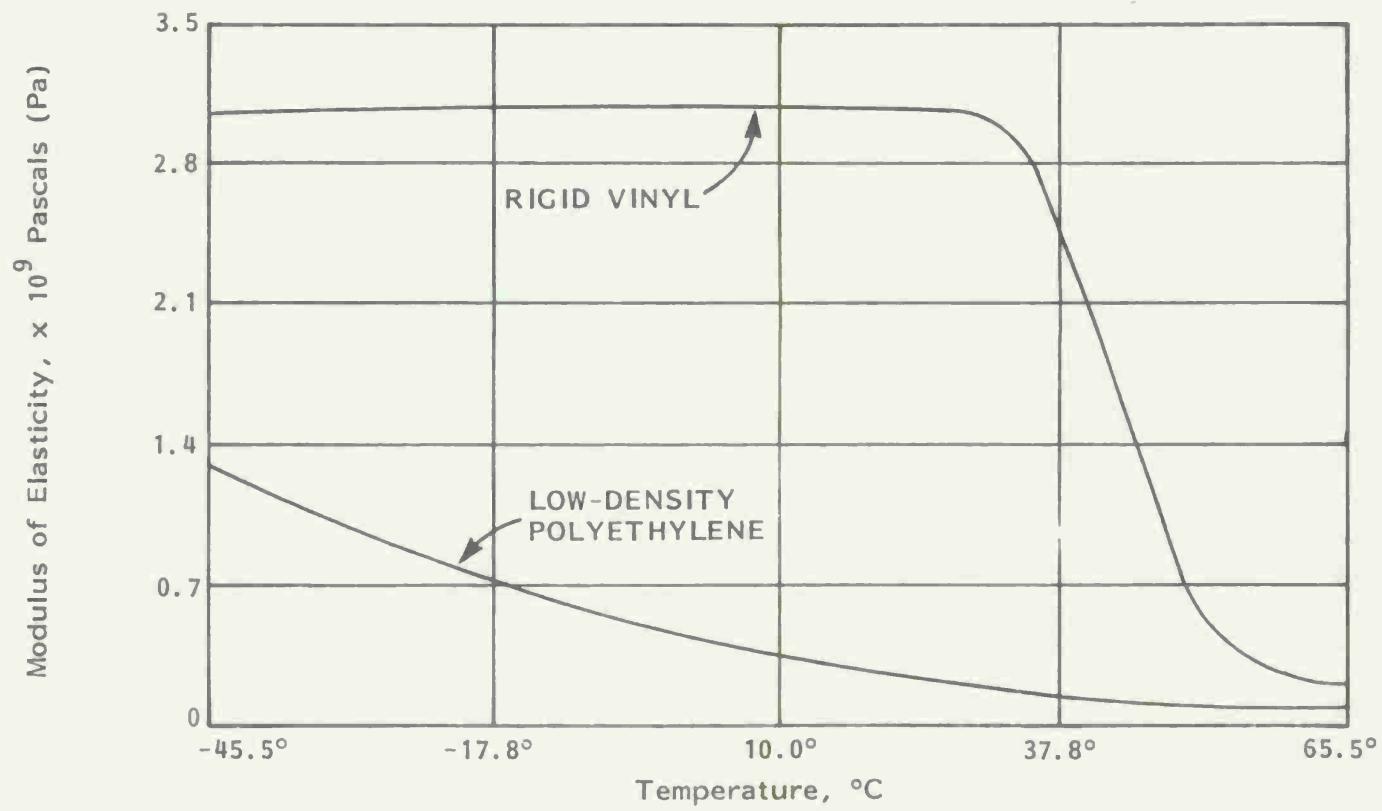


FIGURE 3. MODULUS OF ELASTICITY AS A FUNCTION OF TEMPERATURE

CROSS-LINKED POLYMER

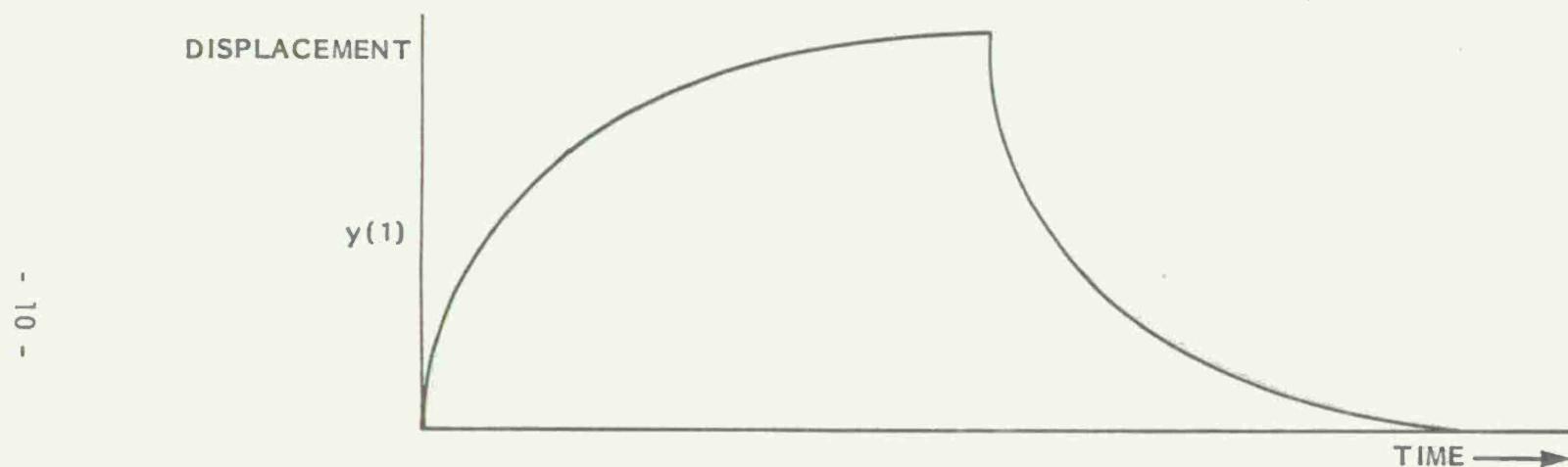


FIGURE 4. CREEP RECOVERY SHOWN SCHEMATICALLY; E.G.,
A CROSS-LINKED POLYMER

UNCROSS-LINKED POLYMER CREEP RECOVERY

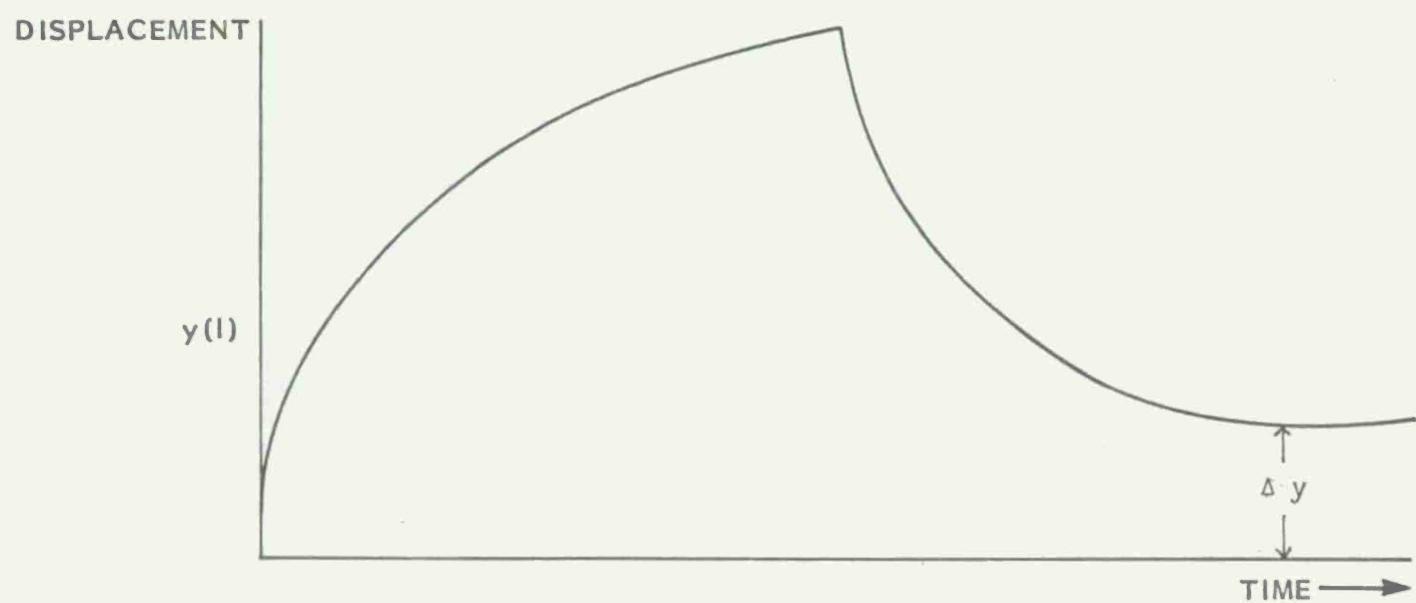


FIGURE 5. CREEP RECOVERY SHOWN SCHEMATICALLY; E.G.,
AN UNCROSS-LINKED POLYMER

Cross-linking increases the ability of the polymer to recover or return to its original form after it has been subjected to a strain. An uncross-linked polymer is less likely to return to its original shape after being subjected to a strain. This property is called the creep recovery of a plastic and is shown for both cross-linked and uncross-linked polymers in Figures 4 and 5. Especially for uncross-linked polymers a permanent deformation could result.

Cross-linking reduces the polymer's susceptibility to chemical attack. Cross-linked polymers are less soluble, swell less than uncross-linked polymers, and are less permeable.

6.4 Frequency or Rate of Strain. The elastic modulus varies as a function of strain rate or frequency of loading. At low frequencies and low strain the two moduli are determined by intermolecular forces and by the polymer chains' ability to reorient themselves. At higher frequencies the polymer chains easily recover and intermolecular forces will predominate.

Another property which varies with frequency is the loss modulus. The loss modulus represents the amount of energy used to compress the polymer that is lost as heat.

6.5 Chemical Resistance. The chemical resistance of a polymer will determine its usefulness in applications. The polymer used in a hydraulic fluid must be compatible with that fluid, metal components, seals, etc. over its operating range. Small amounts of additives in the hydraulic fluid can attack a polymer and destroy its chemical resistivity. As mentioned in Section 6.3, cross-linking decreases a polymer's susceptibility to chemical attack. Crystalline polymers are more insoluble and chemically resistant than amorphous polymers. However, stress and strain can induce small cracks in crystalline polymers which can become pathways for reactions with the atmosphere or liquid surrounding the polymer, and hence, lower the chemical resistance of the polymer.

As with the physical properties, the chemical properties of many polymers have been measured. However, most of the chemical compatibility tests have not been well controlled. The chemical compatibility or chemical resistance for several polymers in four major classes of solvents is given in Table 2. The cautions stated in the beginning of Section 6 are even more applicable in the case of chemical resistance. Many polymers have been tested merely by observing the material after it has been soaked in sheet or film form for several days at room temperature. Rarely is the purity of the fluid specified, and fluid impurities can be responsible for some of the chemical attacks. Sometimes microscopes are used to detect small corrosion marks, etchings, or swelling. Occasionally, the polymer or solvent discolors, and this is

TABLE 2. CHEMICAL RESISTANCE

MATERIAL	CHLORINATED HYDROCARBONS	LIGHT HYDROCARBONS (HEPTANE)	SILICONES (SILOXANES)	FLUORINATED HYDROCARBONS (FREON)	GENERAL COMMENTS
POLYSTYRENE	DG	X	C	COMPATIBLE WITH MOST POLYMERS	Can be used with silicone fluids
POLYETHYLENE (LOW DENSITY)	S	S	S/D		Not compatible with silicone fluids but compatible with hydraulic fluid
POLYVINYL ACETATE	?	C	C(?)		Prone to oxidation and hydrolysis
POLYVINYLCHLORIDE	X	C	C		Prone to oxidation and heat degradation forming HCl and corrosive products
POLYVINYLDENE CHLORIDE	C	C	C		Slow decomposition Recommended with any solvent
POLYMETHACRYLONITRILE	?	?	?		Decomposes and oxidizes forming corrosive products and HCN
POLYMETHYL PENTENE	S	S	?		Unknown, but uncommon (maybe expensive)
POLYPROPYLENE	X	C	?		Attacked by aromatic solvents but compatible with hydraulic fluid. Similar properties to polyethylene (possibly better)
POLYMETHYL METHACRYLATE	X, D	C	S		Attacked by aromatic solvent, non-compressible, swells in water
POLYFLUOROALKYL (TEFLON)	C	C	C		Generally unreactive, self-lubricating
POLYVINYLDENE FLUORIDE	C	C	C		Generally unreactive, self-lubricating

Legend: C - Compatible S - Swelling
 X - Incompatible DG - Degrades and Eventually Fails
 D - Dissolves ? - No Information

indicative that a chemical reaction has taken place. Less frequently, a polymer's tensile strength and other mechanical properties are measured before and after exposure to a fluid. Even when no visual indication of reaction is evident, these latter tests indicate a change in properties which can drastically affect the polymer's performance. The chemical resistance of a polymer may also be affected by the stresses of temperature, pressure, and length of exposure to a fluid. The best indication of a polymer's chemical resistance is to test the type of polymer to be used under the operating conditions for that application.

Table 2 can be used to indicate the probability that a polymer will react with a particular fluid. For example, if polyethylene (PE) swells in heptane, chances are that under stress at 60°C it will be subjected to further attack. However, if polyvinylidene fluoride (PVDF) is compatible with heptane, it should be considered for further testing.

Many polymers containing chlorides decompose to form corrosive by-products. For example, polyvinyl chloride (PVC) oxidizes to produce hydrochloric acid (HCl). These present further potential corrosion problems for most metals. Polyvinylidene chloride (PVDC, SARAN) decomposes to form HCl; however, it does so very slowly. PVDC is worth further consideration because it is compatible with so many materials. Many fluoride polymers, such as PVDC and FEP are very resistant to oxidation and most other chemical reactions. Their chemical inertness, lubricity, and compressibility are characteristics which make them good candidates for future consideration. They are not, however, available as micron-size HPS.

7. CANDIDATE MATERIALS

Materials considered candidates for use in micron-size hollow plastic sphere construction are listed below. The ease or difficulty to produce HPS with the polymers listed is indicated by a rating of one to four: one represents easiest, and four represents most difficult. These ratings were supplied by Rohm & Haas.

1

Polystyrene (PS)
Polymethacrylonitrile (PMAN)
Polymethyl Methacrylate (PMMA)
Polyvinyl Acetate (PVA)

4

Polyvinylidene Fluoride (PVDF)
Polyvinylidene Chloride (PVDC, Saran)
Low Density Polyethylene (LDPE)
Tetrafluoroethylene (PTEE, Teflon)
Polyfluoroalkyl (PFA, Teflon)
Fluorinated Ethylene Propylene(FEP,Teflon)

2

Polyvinyl Chloride (PVC)

3

Polymethyl Pentene (PMP)
Polypropylene (PP)

These polymers were considered as candidate materials because their mechanical properties indicated that acceptable volumetric compressibilities could be attained in HPS, and Rohm and Haas has indicated that their production is possible.

7.1 Mechanical Properties. The mechanical properties of the candidate materials used in compressibility calculations are listed in Table 3. The elastic modulus (E) and Poisson's ratio(ν) of the polymers are important in determining their compressibilities. The values of the elastic modulus and Poisson's ratio are given for 25°C. The melting temperature (T_m) of the polymer and the glass transition temperature (T_g), are in degrees centigrade. Polyvinyl acetate and polyvinyl chloride decompose at their melting temperature and are therefore unstable and inconsistent with this intended use. All of these values are approximate values since the properties will depend on the way in which the polymer is manufactured.

7.2 Equations Relating Mechanical Properties to HPS. The modulus of elasticity (E) is the stress divided by strain. Stress is equal to force (F) divided by area (A). Strain is equal to the elongation (e) divided by length (L).

$$E = \frac{FL}{Ae} \quad \text{Eq. 1}$$

Poisson's ratio (ν) is the ratio of the lateral contraction or deformation(ϵ_x) to the longitudinal or axial elongation (ϵ_y).

$$\nu = \frac{\epsilon_x}{\epsilon_y} \quad \text{Eq. 2}$$

These two basic properties, combined with the dimensions of the HPS and the basic equations for stress on a sphere can be used to calculate the volumetric compressibility of the sphere.

8. COMPRESSIBILITY EQUATIONS

For each of the candidate polymers, the compressibilities of the spheres were calculated as a function of the relative wall thickness and sphere size. The relative wall thickness represented by $A = r/R$ was varied from 0 to 1 simulating the changes from a thick- to thin-walled, hollow plastic sphere.

The basic equation for stress can be modified for the case of a hollow sphere, and used to derive the per cent change in volume (i.e., compressibility) at a given external pressure (P). This derivation is presented in Appendix E.

TABLE 3. MECHANICAL PROPERTIES AT 25°C
(USED IN COMPRESSIBILITY CALCULATIONS)

MATERIAL	ELASTIC MODULUS, E X 10 ⁸ Pa	POISSON'S RATIO, ν	T _M , T _G °C
POLYSTYRENE	35	.33*	238, 100
POLYETHYLENE (LOW DENSITY)	2.4	.46	130, 95-130
POLYVINYL ACETATE	19	.33	150 ¹ , 28-31
POLYVINYLCHLORIDE	25	.38	130 ¹ , 75-105
POLYVINYLDENE CHLORIDE	6.9	.33	210, -18
POLYMETHACRYLONITRILE	41	.33	-, 120
POLYMETHYL PENTENE	14	.33	230-240, -
POLYPROPYLENE	21	.33	168, -
POLYMETHYL METHACRYLATE	31	.33	180, 114
FLUORINATED ETHYLENE PROPYLENE (TEFLON)	5.5	.48	310, -
POLYVINYLDENE FLUORIDE	14	.34	171, 13

* APPROXIMATE VALUES - ν DEPENDS ON HOW THE MATERIAL IS MADE.

¹ MELTS WITH DECOMPOSITION

Equation 3 describes the change in radius (R) for a hollow sphere subjected to an external pressure.

$$dR = \frac{PR}{E} \left[\frac{(1-v)(r^3 + 2R^3) - v}{2(R^3 - r^3)} \right]$$

where: $A = r/R$

R = outside radius, assumed as unity

r = inside radius

dR = change in outside radius

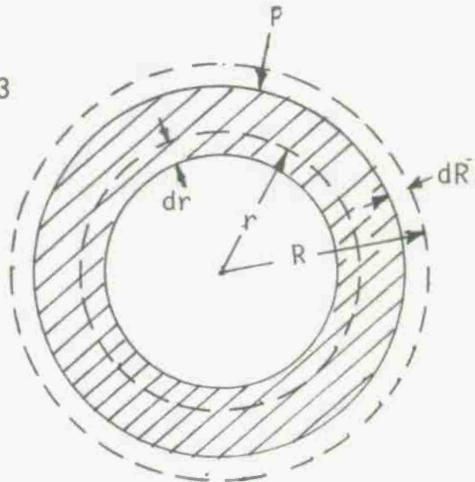
$\%dV$ = per cent change in volume

P = external pressure, Pa

v = Poisson's ratio

E = compressive elastic modulus, Pa

Eq. 3



Equation 3 can be expressed in terms of the ratio of the inner and outer radii ($A = r/R$):

$$dR = \frac{PR}{E} \left[\frac{(2 + A^3)(1 - v)}{2(1 - A^3)} - v \right] \quad \text{Eq. 4}$$

And finally, the volumetric compressibility of the sphere is given as:

$$\%dV = \left[\frac{R^3 - (R - dR)^3}{R^3} \right] \times 100 = \left[1 - (1 - dR)^3 \right] \times 100 \quad \text{Eq. 5}$$

In deriving these equations, the pressure inside the sphere was assumed to be zero.

8.1 Mathematical Analysis. Utilizing the above formula and the characteristic mechanical properties of each polymer at 25°C, mathematical analyses were performed for four of the candidate polymers:

- Low Density Polyethylene
- Polystyrene

- Polyvinylidene Chloride
- Fluorinated Ethylene Propylene, Teflon, Copolymer.

The calculations were performed for an external pressure of 3.5×10^7 Pa, the pressure expected in the fluid recoil mechanism. The results of these calculations are presented in Tables 4, 5 and 6 and are depicted in Figure 6.

8.2 Polymer Compressibility. Several general comments can be made about the behavior of the compressibilities of HPS as calculated.

- In order to obtain the maximum compressibility for the pressure change from 0 to 3.5×10^7 Pa, a relatively low elastic modulus (less than 5.5×10^9 Pa) and an A value (r/R equal to or less than .9) are necessary to prevent buckling and/or permanent deformation of the HPS.
- The effects of Poisson's ratio becomes progressively dominant as the HPS wall thickness increases. As A approaches 0, i.e., as the wall thickness increases so that the sphere is no longer hollow, the sphere's compressibility approaches to 0. When the value of the Poisson's ratio approaches a minimum of 0.25 and A approaches 0, the polymer's strain capacity becomes greater. (See Table 6.)
- As the wall becomes thinner and A approaches 1, the validity of the volumetric compressibility calculations become increasingly less valid.
- Referring to Figure 6, it can be seen as the HPS wall thickness becomes thinner (A value increases), the per cent compressibility (%dV) increases for each polymer within the valid range of the equations. The curves depicted in Figure 6 are relatively accurate between 0 to 12% dV, (4% dR). From 13 to 38% dV the curves become progressively less accurate to predict HPS compressibility.
- HPS constructed of polyvinylidene chloride and low density polyethylene are expected to show good compressibility characteristics with relatively thick wall construction. For example, comparing the polymers at A = .5, polyethylene compressibility is over 8 per cent and polyvinylidene's compressibility is approximately 7 per cent, whereas, FEP, Teflon, and polystyrene's compressibilities are approximately 3 per cent and 1 per cent, respectively.
- Each of the polymers, with the exception of low density polyethylene, shows relatively little change in compressibility below the A = .4 value.

TABLE 4. COMPRESSIBILITY CALCULATIONS FOR LOW-DENSITY POLYETHYLENE AND POLYSTYRENE

$$E = 2.4 \times 10^8 \text{ Pa}$$

$$P = 3.5 \times 10^7 \text{ Pa}$$

$$v = .46$$

LOW DENSITY POLYETHYLENE

A	A^3	dR	$dV (\%)$
.1	.001	.0115	3.42
.2	.008	.0124	3.67
.3	.027	.015	4.43
.4	.064	.019	5.59
.5	.125	.030	8.73
.6	.216	.043	12.35
.7	.343	.072	20.09
.8	.512	.133	34.83
.85	.614	.195	47.83
.9	.729	.323	68.97

$$E = 3.5 \times 10^9 \text{ Pa}$$

$$P = 3.5 \times 10^7 \text{ Pa}$$

$$v = .33$$

POLYSTYRENE

A	A^3	dR	$dV (\%)$
.1	.001	.0034	1.02
.3	.027	.0037	1.11
.5	.125	.0048	1.43
.6	.216	.0062	1.85
.7	.343	.0086	2.56
.8	.512	.0139	4.11
.9	.729	.0304	8.84

TABLE 5. COMPRESSIBILITY CALCULATIONS FOR POLYVINYLDENE CHLORIDE AND FLUORINATED ETHYLENE PROPYLENE (FEP), TEFLON, COPOLYMER

$$E = 6.9 \times 10^8 \text{ Pa}$$

$$P = 3.5 \times 10^7 \text{ Pa}$$

$$\nu = .33$$

POLYVINYLDENE CHLORIDE

A	A^3	dR	dV (%)
.1	.001	.0170	5.01
.3	.027	.0183	5.39
.5	.125	.0241	7.03
.6	.216	.0307	8.93
.7	.343	.0430	12.35
.8	.512	.0694	19.40
.9	.729	.1514	38.89

$$E = 5.5 \times 10^8 \text{ Pa}$$

$$P = 3.5 \times 10^7 \text{ Pa}$$

$$\nu = .48$$

FLUORINATED ETHYLENE PROPYLENE, (FEP), TEFLON, COPOLYMER

A	A^3	dR	dV (%)
.1	.001	.0025	.763
.3	.027	.0039	1.165
.5	.125	.0095	2.823
.6	.216	.0159	4.695
.7	.343	.0279	8.153
.8	.512	.0536	15.246
.9	.729	.1336	34.964

TABLE 6. INFLUENCE OF RADIUS RATIO (A) AND POISSON'S RATIO (ν), ETC., ON RADIAL DISPLACEMENT (dR) OF HPS

A	$\left[\frac{2 + A^3}{2(1 - A^3)} (1 - \nu) - \nu \right]$					
	$\nu = .5$	$\nu = .45$	$\nu = .40$	$\nu = .35$	$\nu = .33$	$\nu = .25$
1.0						
.9	2.018	2.319	2.621	2.923	3.044	3.526
.8	0.787	0.966	1.144	1.323	1.394	1.680
.7	0.392	0.531	0.670	0.809	0.865	1.087
.6	0.207	0.327	0.448	0.569	0.617	0.810
.5	0.107	0.218	0.329	0.439	0.484	0.661
.4	0.051	0.156	0.262	0.367	0.409	0.577
.3	0.021	0.123	0.225	0.327	0.368	0.531
.2	0.006	0.107	0.207	0.308	0.348	0.509
.1	0.001	0.101	0.201	0.301	0.341	0.501
0	0.000	0.100	0.200	0.300	0.340	0.500

NOTE:

The above table shows the effect that the Poisson's ratio (ν) and the radius ratio (A) have on the change in external radial displacement (change in outside radius)-(dR), and, hence, on the compressibility of a hollow sphere. To demonstrate this, only the second part of the Equation 4 for the change in external radial displacement,

$$dR = \frac{PR}{E} \left[\frac{(2 + A^3)(1 - \nu) - \nu}{2(1 - A^3)} \right]$$

has been used. The radius ratio (A) was varied from 0.0 to 1.0 in one tenth increments, and six selected values for ν were used. The results show that as A increases and ν decreases the radial displacement, dR, increases. Furthermore, for a given pressure, P, and a particular value of A and ν , the radial displacement increases as the elastic modulus (E) decreases.

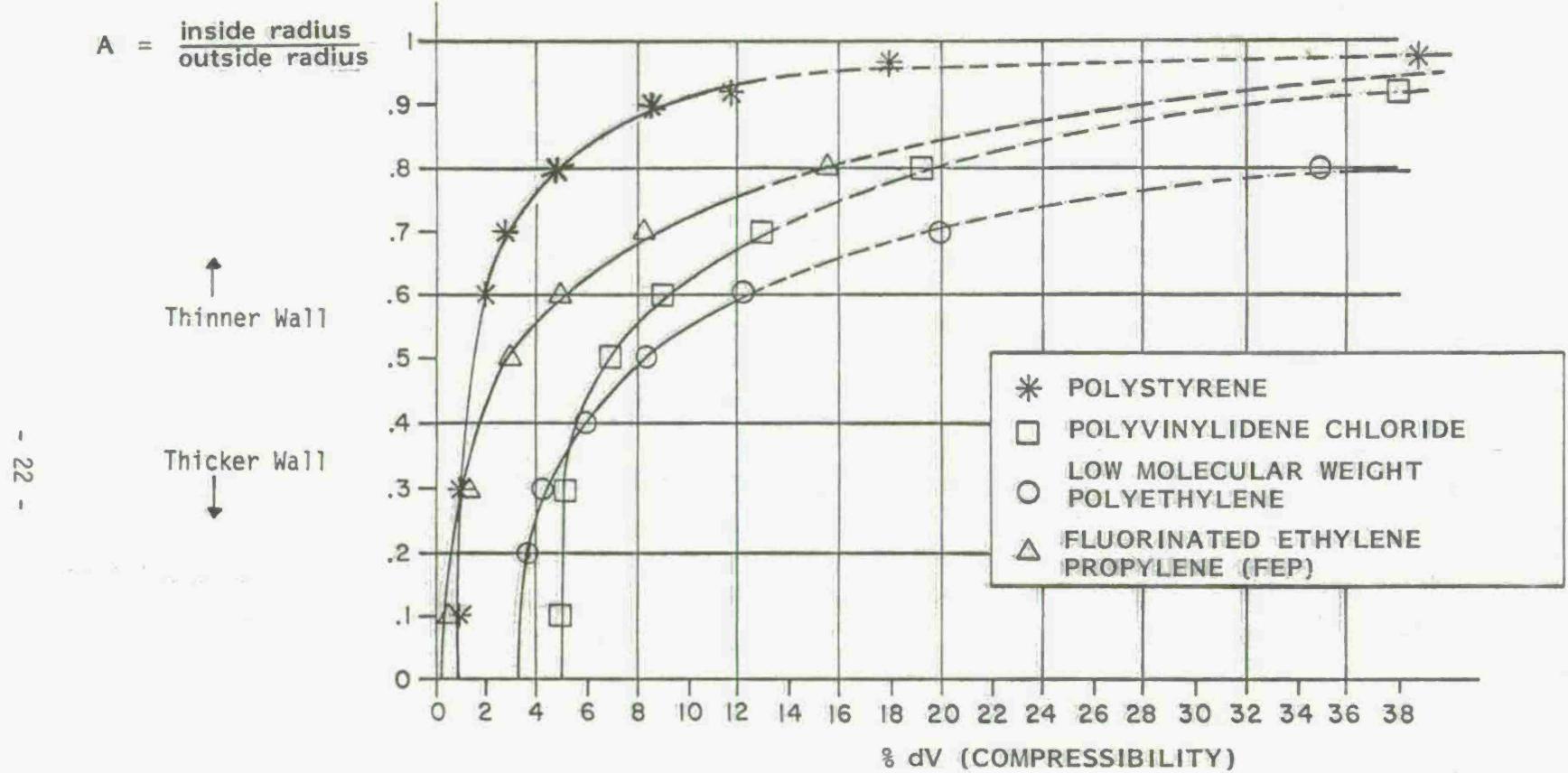


FIGURE 6. CALCULATED COMPRESSIBILITY AS A FUNCTION OF WALL THICKNESS

9. RECOMMENDATIONS AND CONCLUSIONS

The recommendations and conclusions of this feasibility study are separated into those resulting from the engineering analysis of compressibility of HPS and those from chemical considerations of the structure of polymers.

9.1 Engineering Analysis. The engineering analysis of the compressibility of a hollow plastic sphere is intended to serve as a guide for selecting suitable polymers for HPS usage. It is an indication of HPS compressibility when suspended in fluid and subjected to hydraulic pressure. Actual HPS compressibility degradation, longevity, consistent reproducibility of energy storage, under repeated firing conditions, will have to be determined through a comprehensive experimental testing program. Data obtained from these experiments will need to be analyzed and related to the mechanical properties of the tested polymers. These tests will form the basis of subsequent choices of polymer materials. These tests will most readily be performed on the polystyrene spheres which can be obtained from Rohm and Haas. Polystyrene spheres with a radius ratio $A = 0.9$, are predicted by a simplified model presented here to have a compressibility of 8.84% at 3.5×10^7 Pa. When these HPS are added to the silicone fluid, the increase in total recoil will be proportional to the volume of fluid occupied by the HPS.

9.2 Chemical Considerations. In general, if flexibility is the most important attribute, the polymers chosen should be amorphous, with T_g less than the operating temperatures to insure that the amorphous state rather than the glassy crystalline state predominates. To insure flexibility and lack of surface crystals, the polymer should not be cured. Amorphous polymers are not very chemically resistant, however, and may be permanently deformed. If an appropriate amorphous polymer cannot be found, a crystalline polymer would be the second choice.

Knowledge of the additives to both the polymers and the fluids considered will help to determine the chemical compatibility of the systems. In addition, additives to the polymer can hinder its production as hollow plastics spheres in the micron and sub-micron size range.

Table 7 lists some of the polymers recommended for further study. FEP(Teflon) and PVDF are crystalline polymers chemically inert to most fluids and for that reason are good choices for further tests. FEP (Teflon) and PVDF are also self-lubricating

TABLE 7. POLYMER RECOMMENDATIONS

Based on their physical and chemical properties, these polymers are recommended for further study.

<u>POLYMER</u>	<u>CHARACTERISTICS</u>
Fluorinated Ethylene Propylene (FEP, Teflon)	Very stable, self-lubricating non-corrosive, unreactive
Polyvinylidene Fluoride (PVDF)	Same as Teflon
Polystyrene (PS)	Available as hollow plastic spheres, compatible with silicone fluids, rigid and glass-like
Polyethylene (PE)	Most compressible of investigated polymers, flexible even at low temperatures
Fluorosilicon	Teflon-type polymer
Polyvinylidene Chloride (PVDC)	Compressible and flexible, chemically resistant in most environments, decomposes slowly

polymers, which will be an advantage to using them with moving parts. DuPont Chemical Corporation produces a powder, DLX-600, made of non-spherical particles, less than 10^{-6} meter in diameter. Even though it is not a hollow plastic sphere, it may serve the purpose of increasing the compressibility of the fluid.

In the operating temperature range polystyrene is glass-like and rigid. It is not very compressible and will probably behave as most glasses under stress, i.e., be subject to cracking and shattering. Although it can be made as small hollow plastic spheres, when added to a fluid, polystyrene is not as likely to increase the compressibility of the fluid to the desired degree as more compressible polymers are.

9.3 Conclusions. It is important to recognize the two major limitations of these first sets of experiments:

- The polystyrene is not very compressible according to the engineering analysis.
- The concept of suspending the micron-size spheres in the silicone fluid is being tested. Failure of the HPS to dramatically increase the compressibility of the silicone fluid is not a failure of the concept being tested.

In evaluating the performance of the polystyrene HPS and silicone fluid mixture, the evaluation must distinguish between the results due to the separate aspects of the polystyrene HPS properties which may affect the performance of the fluid. These include the brittleness and compressibilities of the spheres. Thus, if the tests show that the compressibility of the fluid was not increased, but that in all other respects the fluid performs well, the concept of suspending HPS in the fluid has been demonstrated. The next set of experiments should then focus on testing more compressible polymers.



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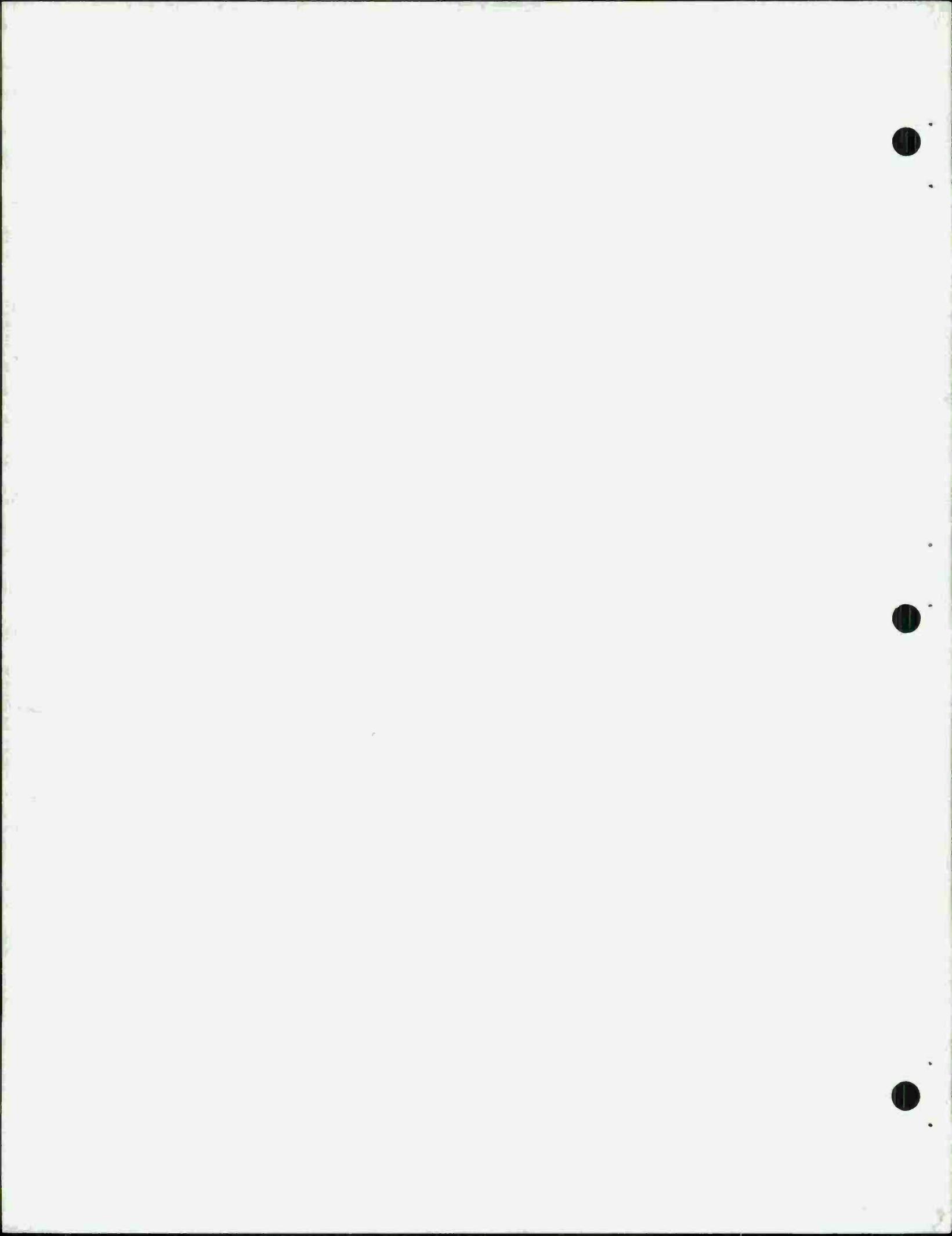
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APPENDIX A
U.S. COMPANIES CONTACTED

<u>COMPANY</u>	<u>PHONE</u>	<u>ADDRESS</u>
3M Corp.	612-733-1306	3M Center, St. Paul, Minn.
P.O.G. Ind. Inc.	412-434-2583	Pittsburgh, Penn.
Westlake Plastics Co.	215-459-1000	Lenni, Penn.
Rohm & Haas Co.	215-641-7000	Philadelphia, Penn.
Uniroyal Chemical Co.	203-723-3849	Naugatuck, Conn.
Amoco Chemical Corp.	312-856-3528	Chicago, Ill.
Emerson & Cumming	617-828-3300	Canton, Mass.
Montedison U.S.A. Inc.	212-764-0260	N.Y., New York
Cadillac Plastics & Chem Co.	800-521-4004	Birmingham, Mich.
Adell Plastics Inc.	301-789-7780	Baltimore, MD
DuPont De Nemours, E.I. & Co.	302-774-2421	Wilmington, Del.
B.F. Goodrich	216-447-6000	Cleveland, Ohio
American Cyanamid	201-831-2000	Wayne, N.J.
Celanese Plastics	201-635-2600	Chatham, N.J.
Uniroyal	203-723-3000	Nauyatab, CT
Olin Corp. Chem. Div.	203-356-2525	Stanford, CT
P.D. George Co.	314-621-5700	St. Louis, Mo.
Upjohn Polymer & Chem. Div.	713-979-1541	La Porte, TX
Argus Company	212-858-5678	Brooklyn, N.Y.
Durez Div. of Hooker Chem.	716-696-6234	New York, N.Y.
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Union Carbide	404-633-6161	Atlanta, CA
American Polymer's Inc.	201-345-0020	Paterson, N.J.
Hercules Inc.	302-575-6500	Wilmington, Del.
Fiberfil Div.	812-424-3831	Evansville, Ind.
Saltamer Co. Div.	215-692-8400	Westchester, Penn.
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Shell Chemical Co.	713-241-6161	Houston, TX
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Grace, W.R. & Co.	617-861-6600	Lexington, Mass
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Shuman Plastics, Inc.	716-685-2121	New York, N.Y.
Stan Chemical, Inc.	203-828-0571	E. Berlin, Conn.
Union Oil Co. of Cal.	312-885-5627	Schaumburg, Ill.
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Georgia Pacific Corp.	516-694-8252	Farmingdale, N.J.

APPENDIX B

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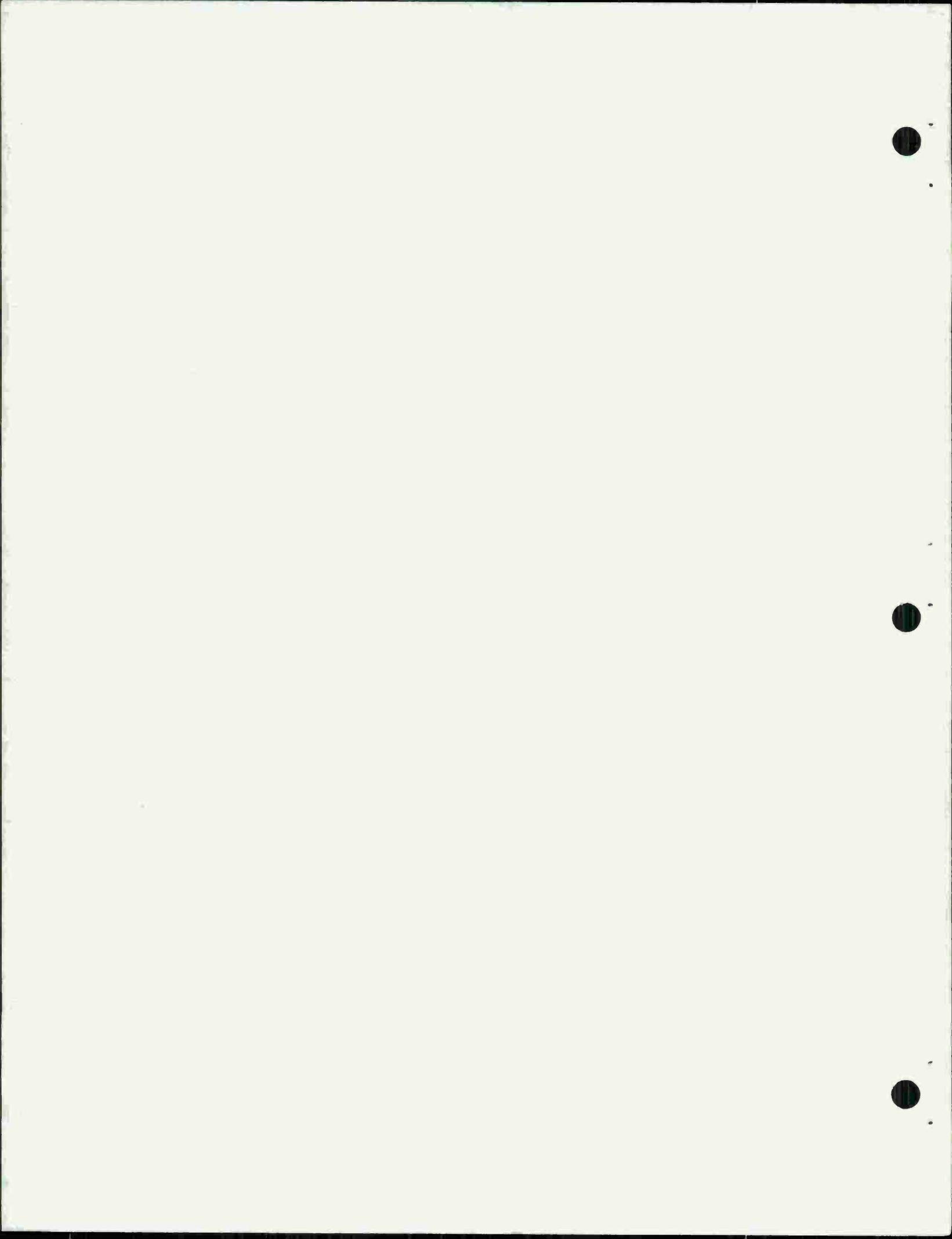
<u>COMPANY</u>	<u>ADDRESS</u>
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Expladan A/S	Industrivej 22, 4652 Haarlev, Denmark
Maersk Kemi A/S	Klovermarksvej 70-2300 Copenhagen S, Demark
Abeco Ltd.	Timber Lane-Waburn MK17 9P1, England
Yardley Plastics Ltd.	Caddick Road-Knowsley Ind. Knowley Prescot L34,9HB England
Shell Chemicals (UK) Ltd.	No. 1 Northumberland Ave.-Trafalger Square London WC2N SLA England
Ellesmere Thermoplastics Ltd.	Siemans Road-Off Brinell Drive Northbank Ind. Estate, Cadishe, England
British Celanese Ltd.	Celanese House 22-23 Hanover W1A 1BS England
Belgrave Northwestern Ind. Ltd.	Hawthorne Road-Bostle L20 6JT, England
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Sikema AB	Nybohorsgrand 9 Box 9208 S-102-73 Stockholm, Sweden
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Dow Chemical AB	Karlov 53, S-114,49 Stockholm, Sweden
Kodama Chemical Ind. Co. Ltd.	Seiko Bldg., 703, Sotokanda 6-chome Chiyoda-Ku, Tokyo 101, Japan
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Victor Wolf Ltd.	Clayton Lane Clayton-Manchester M11 4SR, England
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Peritek Shell Nederland Chemie B.V.	P.O.B. 1092, 3180 AB Rozenburg- Netherlands P.O.B. 7005, 3000 AH Rotterdam, Vondelingenweg 601, Rotterdam, Netherlands
Rotterdamse Polyolefinen ICC Industries B.V.	P.O.B. 7015, 3000 HA Rotterdam, Netherlands P.O.B. 7000, 1007 MA Amsterdam, Amsteldijk 166, 1079 LH Amsterdam, Netherlands
Ciago B.V.	P.O.B. 299, 6880 AG Velp, 6883 AK Velp, Netherlands
N.V. DSM San Ho Plastics Fabrication Lordland Plastics Manufacturing	P.O.B. 65, 6400 AB Heerlen, VP Heerlen, Netherlands 40 Min Chuan W. Rd. Taipei Taiwan, R.O.C. 6th Fl., 29, Chung-shen N. Rd., Sect. 3 Taipei, Taiwan
K.E. & Kingstone Co., Ltd.	7th Fl., 129 Sung Chiang Rd. Taipei, Taiwan R.O.C.

APPENDIX B
FOREIGN COMPANIES CONTACTED (CONTINUED)

<u>COMPANY</u>	<u>ADDRESS</u>
Fairmost Ind. Co., Ltd.	4th Fl., 8-1, Hong Chou S. Rd., Sec. 1 Taipei, Taiwan, R.O.C.
Digest International Development Corp.	129,Surs Chiang Rd. Taipei, Taiwan, R.O.C.
Star Light Products Co.	P.O.B. 53318, Taipei, Taiwan, R.O.C.
Nan Ta Ind. Co., Ltd.	Sung Chaing Rd. Taipei, Taiwan, R.O.C.
Lead Enterprise Company	How Kow St., Sec. 2 Taipei, Taiwan, R.O.C.
Ghin Der Plastic Ind. Co.	P.O.B. 70-13 Taipei, Taiwan, R.O.C.
Eternal Chem Co. Ltd.	220 Chien Kung St. Kaohsiung, Taiwan,R.O.C.
Poly Chemical Co. Ltd.	2-1 Chung Cheng Rd. Jen Te. Taiwan, R.O.C.
Ram Plastics Corp.	P.O.B. 186 Concord Ontario, Canada
Plastiques GM Ltd.	St. Hubert, Quebec J34 St. 7 Canada
Rochevert, Inc.	451 Veanrie-Mance St. Valley Field, Quebec V6T 4G2 Canada
Polysar Limited, Kayson Plastics Div.	Cambridge, Ontario N3H 4T6 Canada
Canlew Chemicals, Ltd.	7435 Chester Ave. Montreal, Quebec H4V 1M4, Canada



APPENDIX C
U.S. AND FOREIGN COMPANIES-RESPONDING

<u>No.</u>	<u>Company</u>	<u>Phone</u>	<u>Address</u>	<u>Comment</u>
1.	Dow Chemical AB		2-114-49, Stockholm, Sweden	Recommended their Mother Co. in Midland, MI.
2.	3M Corporation	612-733-0306	3M Center, St. Paul, MN	Manufacture HPS, but could not control the dimensions & wall thickness.
3.	P.P.G. Ind. Inc.	412-434-2583	Pittsburg, PA	Manufacture HPS, but could not control the dimensions & wall thickness.
4.	Westlake Plastics Co.	215-259-1000	Lenni, PA	Recommended Union Carbide.
5.	Rohm & Haas	215-641-7000	Philadelphia, PA	Manufacture HPS-Possible candidate.
6.	Uniroyal Chemical Co.	203-723-3849	Naugatuck, CT	Does not manufacture HPS-sent brochures.
7.	Amoco Chemical Corp.	312-856-3528	Chicago, IL	Sent data on high performance polymers.
8.	U. S. Industrial Chemicals Co.		Dallas, TX	Technical data on polyolefins or injection molding.
9.	Emerson & Cumming	617-828-3300	Canton, MA	Manufacture HPS, but they could not control the dimension & wall thickness.
10.	Puren-Schaumstaff GmbH	64055-56	7770 Überlingen, Germany	Manufacture of polyurethane hard foam.
11.	Poly Form		Rue Joe Wauters 80 4830 Limbourg, Belgium	Recommend Floridiene (S.A.)

APPENDIX C

U.S. AND FOREIGN COMPANIES - RESPONDING(CONTINUED)

12	Malmsten & Bergrall AB		P.O. Box 48S-401 20 Gofeborg	Not in the business of Hollow Plastic Spheres
13	Thuysbaert N.V. (S.A.)	031/37.31.86	B-2020 Antwerp , Belgium	Transferred letter to F.I.C.B. Belgium.
14	Sikema (AB)	08-180270	P.O. Box 9208, Stockholm,Sweden	Not active in the field of HPS.
15	Montedison U.S.A. Inc.	212-764-0260	N.Y., New York	Not active in the field of HPS.
16	Cadillac Plastics & Chem Co.	800-521-4004	Birmingham, MI	Does not manufacture HPS.
17	Adell Plastics Inc.	301-789-7780	Baltimore, MD	Does not manufacture micron size Hollow Plastic Spheres.
18	DuPont De Nemours, E.I.&Co.	302-774-2421	Wilmington, DE	Work in the area of Polyurethane.
19	B.F. Goodrich	216-447-6000	Cleveland, OH	Not in the business of Hollow Plastic Spheres.
20	American Cyanamid	201-831-2000	Wayne, NJ	Manufacture of polyurethane hard foam
21	Celanese Plastics	201-635-2600	Chatham,NJ	Not active in the field of HPS
22	Olin Corp. Chemicals	203-356-2525	Standford, CT	Active in the field of polyurethane.
23	P.D. George Co.	314-621-5700	St. Louis, MO	Polymide;not active in the field of HPS
24	Upjohn Polymer & Chem Div.	203-281-2700	North Haven, CT	Polyurethane manufacture
25	Argus Company	212-858-5678	Brooklyn,NY	Not in the business of Hollow Plastic Spheres
26	Durez Div. of Hooker Chem	716-696-6234	New York, NY	Sent information on phenolics
27	Casden Oil & Chemical	214-750-2800	Dallas, TX	Recommended Mel Pate,Tech. Group, 312-862-6140
28	Dow Corning	800-248-2345	Midland,MI	Manufacture Dow Corning 300 Fluid; polystyrene

APPENDIX C
U.S. AND FOREIGN COMPANIES - RESPONDING (CONTINUED)

29	U.S.I Chemicals	214-387-1130	Dallas, TX	Not in the business of Hollow Plastic Spheres
30	Richardson-Tech. Services	800-243-4750	Enfield, CT	Manufacture styrene & methyl methacrylate
31	Union Carbide	404-633-6161	Atlanta, GA	Manufacture microballoons (phenolic) but could not control dim. & wall thickness
32	American Polymers Inc.	201-345-0020	Patterson, NJ	Does not manufacture Hollow Plastic Spheres.
33	Hercules Inc.	302-575-6500	Wilmington, DE	Not in the business of Hollow Plastic Spheres.
34	Fiberfil Div.	812-424-3831	Evansville, IN	Received information package; not active in the field of HPS
35	Saltomer Co. Div.	215-692-8400	Philadelphia, PA	Sent information not involved with Hollow Plastic Spheres
36	R.A. Chem. Inc.	212-859-2800	NY, NY	Not involved with Plastics
37	Expladan A/S		Denmark	Sent information package; but no reply.



APPENDIX D

REFERENCES

KEY WORDS

polymer	thermoplastic	shells	deformation	thermal properties
plastic	strain (rate)	stress	compression	mechanical properties
elastomer	polymerization	strain	energy	bulk modulus
resin	sphere	analysis	distortion	Poisson's ratio
thermoset	micropalloons	study	physical properties	polymer chemistry
polymer matrix	polymer physics	fluoropolymers	high polymers	spherical shells
spheroids	hollow	thick wall	polymer properties	proportional limits
oil, fluid	oil, additives	olefins	hydraulic fluid	compressible fluid
compressibility	compressibility effects	bouyancy	viscoelastic	polymer structure

SUBJECT UTILIZATION

SUBJECT

Polymers, plastics
and elastomers

Engineering characteristics
of selected polymers

RESULTS

- Rheology of numerous polymers
 - Candidate HPS materials selected and evaluated
 - Crystalline versus amorphous structures
 - Glass transitional temperatures, T_g
 - Melting temperatures, T_m
 - Creep
 - Chemical resistance
 - Compatibility with fluids
 - Heat and chemical degradation.
-
- Stress
 - Strain
 - Compressibility
 - Mechanical properties
 - Poisson's ratio
 - Bulk modulus
 - Elastic modulus
 - Hollow sphere circumferential loading equations
 - Formula derivations.

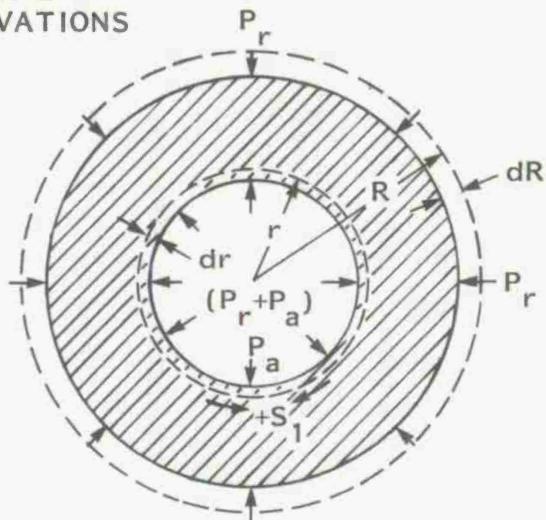
APPENDIX D
REFERENCES (CONTINUED)
RESULTS OF COMPUTER LITERATURE SEARCH

NASA/Recon (Computer Data Base)		NUMBER OF LITERATURE REFERENCES RELATED TO HPS FEASIBILITY STUDY	Dialog Information Retrieval Service	
KEY WORDS	NUMBER OF LITERATURE REFERENCES AVAILABLE		KEY WORDS	NUMBER OF LITERATURE REFERENCES AVAILABLE
<u>polymers</u>	3693	42	polymer	8549
polymerization	2310	10	plastic	14387
polymer chemistry	1414	3	elastomer	1801
polymer matrix				
composite materials	367	12	resin	6254
polymer physics	1064	3	thermoset	233
elastomers	1689	14	thermoplastic	580
fluoropolymers	55	11	strain (rate)	515
high polymers	140	1	polymerization	2259
<u>spheres</u>	3333	23	sphere	3660
- 42 spherical shells	1944	11	microballoons	12
spheroids	364	8	shells	0
hollow	54	3	stress	14470
thick wall	414	8	strain	7180
<u>polymer properties</u>	65	23	analysis	126,952
proportional limits	104	7	study	667
<u>mechanical properties</u>	0	0	deformation	8049
<u>physical properties</u>	0	0	compression	2269
<u>thermal properties</u>	0	1	energy	42810
<u>oil fluid</u>	0	0	distortion	1670
oil additives	150	1	physical properties	5906
olefins	0	1	mechanical properties	9594
hydraulic fluid	684	10	thermal properties	2783
compressible fluid	1087	11	bulk modulus	70
compressibility	638	12	Poisson's ratio	377
compressibility effects	783	11		
<u>bulk modulus</u>	174	3		
buoyancy	934	12		

APPENDIX E
FORMULA DERIVATIONS

HOLLOW PLASTIC SPHERES (HPS)

The derivation of formulas for determining radius ratio $A(r/R)$, inner displacement (dr), and outer displacement (dR) of HPS due to external pressure (P_r), assuming internal pressure (P_a) = 0, with $P = P_r + P_a$.



RADIUS RATIO $A(r/R)$

Since the maximum compressive stress occurs on the inner surface, radius (r), the equation for stress (S_1) is used in determining $A(r/R)$; $+ S_1$ = compressive stress.

$$1. \quad S_1 = P \frac{3R^3}{2(R^3 - r^3)}$$

Let $A = r/R$; Radius Ratio, $A = \frac{\text{inner radius (}r\text{)}}{\text{outer radius (}R\text{)}}$
 $r = AR$

$$2. \quad S_1 = \frac{3P}{2(1-A^3)} \quad \text{Solving for } A$$

$$3. \quad A^3 = \left(1 - \frac{3P}{2S_1}\right); \quad A = \left(1 - \frac{3P}{2S_1}\right)^{1/3}$$

Assuming the internal pressure (P_a) is 0, the external radial displacement (dR) is given as:

$$4. \quad dR = \frac{PR}{E} \left[\frac{(1-v)(r^3 + 2R^3)}{2(R^3 - r^3)} - v \right]$$

Substituting $r = AR$ in equation 4.

$$5. \quad dR = \frac{PR}{E} \left[\frac{(2+A^3)(1-v)}{2(1-A^3)} - v \right]$$

Volume change (dV), due to external pressure (P_r)

$$dV = \frac{4\pi}{3} [R^3 - (R-dR)^3]$$

The per cent volume change due to the external pressure (P_r)

$$dV = \frac{4/3\pi}{4/3\pi R^3} \left[R^3 - (R-dR)^3 \right] (100) = \frac{R^3 - (R-dR)^3}{R^3} (100)$$

$$dV = \left[1 - (1-dR)^3 \right] 100$$



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